to form perfect monolayer structures, most probably because of insufficient length of its hydrocarbon chain.[11]

In conclusion, experimental evidence has been provided demonstrating the feasibility of the multilayer assembling procedure outlined in Scheme I. Though not perfect, the present multilayer films are first examples of artificial planned structures of this type realized exclusively by chemical means. Besides its theoretical significance, this "chemical approach" might offer, if optimized, important practical advantages over the classical LB method.

Bridging Ligand Effects in Quadruply Bonded Dichromium(II) Compounds

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Most quadruply bonded dichromium(II) compounds can be divided into two different groups.[1] The first group is characterized by the presence of four carboxylato ligands, some interaction in the axial position, and a Cr–Cr bond length ranging from 2.283 to 2.541 Å, while the second group is characterized by ligands derived from weaker acids, infrequent axial interactions, and Cr–Cr bond lengths of less than 1.90 Å. The wide range of Cr–Cr bond lengths has been attributed to two factors.[2] Of these two factors, the effect of the axial interaction has been investigated experimentally.[1-8] The inductive effect of the bridging ligand, however, has not been investigated as thoroughly, although experiments are presently underway.[9] We have used generalized molecular orbital (GMO) and configuration interaction (CI) calculations on tetrakis(formato)dichromium and tetrakis(formamidato)dichromium to investigate this problem. Our calculations predict that the latter has a much stronger Cr–Cr bond.

The GMO method[10] consists of a multiconfiguration self-consistent field calculation followed by a CI calculation. All of the orbitals are kept doubly occupied except for those involved in the quadruple bond. For the eight electrons in the quadruple bond, the GMO wave function consists of the dominant single determinant (σ^2, π_x^2, π_y^2, δ^2) plus all paired double excitations, from these bonding orbitals to their antibonding counterparts (σ^*, π_x^*, π_y^*, δ^*), weighted equally.[10] Application of the variation principle yields a set of primary orbitals (σ, π_x, π_y, δ, σ^*, π_x^*, π_y^*, δ^*) in which the weakly occupied ones (σ^*, π_x^*, π_y^*, δ^*) are optimized to correlate the strongly occupied ones (σ, π_x, π_y, δ). The determination of the GMO orbitals is then followed by a full CI calculation in this restricted orbital space.

Because of the size of the dichromium systems, some additional approximations have been made. We have limited the study to two simple ligand systems, the tetrakis(formato)dichromium and the tetrakis(formamidato)dichromium. The bond distances and angles for the two systems are shown in Figure 1 and are based on average values compiled from a number of known carboxylato and carboxyamidato species.[2-4,11,12] The symmetry of the tetrakis(formato) species is D_{4h} while the symmetry of the tetrakis(formamidato) species is D_{2d} since the nitrogens are trans to each other. Even with this reduction in the size of the system, we have not been able to employ a very large basis set. The basis set consists of fully contracted functions on the ligands and the chromium core. The outer d function on the chromium has been split to give a double ζ representation in order that we might have a better description of the chromiums. Additional s and p functions have been added to represent the 4s and 4p orbitals with exponents of 0.10 and 0.15, respectively.

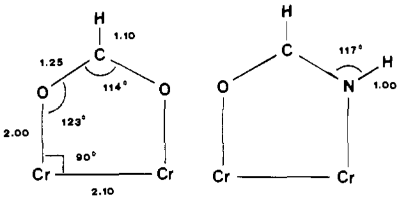

Figure 1. Structure of dichromium model compounds. The bond distances and angles given for the tetrakis(formato) species apply for the tetrakis(formamidato) species, as well.

Table I

	$Cr_2(O_2CH)_4$	$Cr_2(NH(O)CH)_4$
	Orbital Occupations	
σ	1.6	1.7
π	2.8	3.5
δ	1.3	1.5
δ^*	0.7	0.5
π^*	1.2	0.5
σ^*	0.4	0.3
	Important Configurations[a]	
$\sigma^2\pi^4\delta^2$	0.22	0.37
$\sigma^2\pi^4\delta^{*2}$	0.08	0.08
$\sigma^2\pi^2\delta^2\pi^{*2}$	0.16	0.13
$\pi^4\delta^2\sigma^{*2}$	0.02	0.02
	GVB Orbital Overlap Values	
σ	0.32	0.42
π	0.20	0.45
δ	0.13	0.26
	Ratio of d Orbital Coefficients	
σ	0.184	0.227
π	0.196	0.313
δ	0.211	0.272

[a] The values represent the sum of the square of the coefficients corresponding to different spin components of the same configuration.

The results are shown in Table I. In the first part, we have listed the orbital occupation numbers for the two systems. As can be seen, the number of electrons in the bonding orbitals increases upon going from the formato species to the formamidato species, especially in the π orbital. In the second part, we have listed the coefficients of the configurations that make up the ground-state wave function. As shown, the coefficient for the quadruple bond is much larger for the formamidato species than for the formato species. In the third part, we have listed the general valence bond (GVB) orbital overlap values.[13] These values were calculated from our natural orbital occupation numbers.[14] Again, the formamidato species has higher overlap values than the formato species for each orbital.

All three methods of analyzing the CI wave function indicate that the formamidato species has a stronger quadruple bond. One explanation for this effect can be found by examining the radial extent of the d functions on the Cr atoms. At the bottom of Table

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I, we have listed the ratio of the coefficient of the diffuse d orbital to that of the contracted d orbital. For all three orbitals the formamidato species has a higher ratio. Therefore, the d orbitals are expanding more in the formamidato species due to donation from the nitrogen, which leads to better overlap and a stronger quadruple bond.

We will be reporting potential-energy curves for these two compounds as well as calculations on other quadruply bonded dichromium systems in a forthcoming paper. Preliminary results predict an equilibrium bond distance of 2.4 Å for tetrakis(formato)dichromium.

These results indicate that the nature of the bridging ligand strongly affects the strength of the quadruple bond. Thus, the inductive effect of the bridging ligand may determine whether or not axial ligands will bond. It is likely that on species with four carboxylato ligands, the Cr atoms cannot compensate for the loss of electron density when the axial ligands are removed like they can in compounds with very short Cr–Cr quadruple bonds. This is perhaps why the tetrakis(carboxylato) species attract axial ligands so strongly. These results do not mean that the presence of axial ligands is unimportant but that the inductive effects of the bridging ligands are equally important. Thus, if a tetrakis(carboxylato) species without any axial ligands could be synthesized, there might be a decrease in the quadruple bond length, but not enough to move it into the group of compounds with bond lengths less than 1.90 Å.

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Registry No. Cr, 7440-47-3; tetraformatodichromium, 63448-51-1; tetraformamidatodichromium, 84237-52-5.

Low-Temperature Metallic Conductivity in a Metallomacrocyclic Crystal: Nickel Phthalocyanine Iodide

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Only a few molecular crystals exhibit high electrical conductivity down to low temperature,[1-5] and only one has been reported to superconduct at ambient pressure.[6] These few known compounds (Table I) are based on derivatives of organic chalcogenides, and the low-temperature conducting state is stabilized through two- or three-dimensional, chalcogen (S or Se) mediated, interstack interactions. We report here that nickel phthalocyanine iodide, NiPcI,[7] which we earlier found to exhibit metal-like conductivity at temperatures above ca. 50 K,[8] is the first molecular crystal that behaves as a metal down to the lowest available temperature, 100 mK, yet contains neither chalcogen-mediated nor indeed any apparent strong interstack interactions. In addition, it is the first low-temperature molecular metal based on a metal–organic complex.[9]

Table I. Low-Temperature Molecular Conductors

compound^a	σ(room temp), Ω^{-1} cm^{-1}	T_L, K^b	$\sigma(T_L)/\sigma$(room temp)	ref
Ni(Pc)I	~550	0.1	0.5-2	8
HMTSeF-TCNQ	2×10^3	1.1	0.5	2
(TSeT)$_2$X^c	2×10^3	4.2	~1	c
(TMTSeF)$_2$ClO$_4$	~10^3	1.4^d	∞^d	6
(BEDT-TTF)$_2$ClO$_4$	260	1.4	~35	5

^{a} See ref 7 for abbreviations. ^{b} Lowest temperature examined, except as noted. ^{c} X = Cl;[3] X = Br;[3] X = I.[4] ^{d} Superconductive transition, 1.4 K.

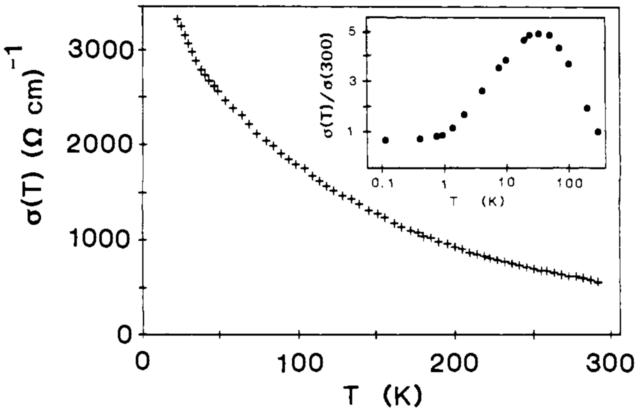

Figure 1. Temperature response to the needle-axis (*c*-axis) conductivity of a NiPcI crystal. Inset: temperature response to the needle-axis conductivity emphasizing the low-temperature behavior; the conductivity has been normalized to the ambient-temperature value of ca. 600 Ω^{-1} cm^{-1}.

The NiPcI crystals (~2 × 0.03 × 0.03 mm) were obtained and EPR measurements carried out as reported previously.[8] Single-crystal conductivity data from 300 to 20 K were obtained by a four-probe ac phase-locked technique described elsewhere.[10] Resistivity measurements down to a temperature of 100 mK as well as magnetoresistance and thermoelectric power measurements were done on previously described apparatus.[11] The crystals were mounted with a conducting palladium paste on thin (8 μm) graphite fibers (Alfa/Ventron) that had been chemically silvered.[10]

The needle (stacking) axis room-temperature conductivity, $\sigma_{\parallel}$, of NiPcI crystals has an average value of ca. 550 Ω^{-1} cm^{-1} and invariably increases with cooling.[8] At low temperature, the four-probe measurements were very crystal dependent, and we ascribed spurious conductivity "transitions" to stress from the relatively thick contact wires; NiPcI crystals are very brittle when cold. A single four-probe measurement and a single, very preliminary, high-frequency contactless measurement coincided in giving a reversible conductivity maximum at 55 K, and therefore we concluded that at about this temperature there was a reversible transition to a state of lowered conductivity. However, upon cooling Ni(Pc)I crystals mounted relatively free of stress through

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